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THE PROPERTIES OF COLUMN PACKINGS CONTAINING SMALL AMOUNTS OF STATIONARY PHASE IN GAS-LIQUID CHROMATOGRAPHY

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SUMMARY

Graphs are presented of the relations between the net retention volume per gram of column packing, V_{N_g} , and the percentage of loading of Polisorb C with the stationary phases *n*-octadecanol and *n*-octadecane. From these relations and the value of the contact angle between the surface of diatomite and solutions of the stationary phases, it is shown that mono- and bimolecular layers of the stationary phase are formed on the support surface. The distribution of the stationary phases on the surface of the support is discussed in terms of the energetics of the support surface.

INTRODUCTION

Column packings in partition gas chromatography usually consist of a liquid stationary phase in contact with the surface of a solid, either that of the support or that of the walls of the capillary column. In such columns, the retention time is dependent primarily on the interactions between the molecules of the solute and those of the stationary phase. The mechanism of dissolution of the solute in the stationary phase is sometimes complicated by the simultaneous phenomenon of adsorption at the interface between the phases in the chromatographic system. The processes of retention of a solute on the column are described by the well known equation

$$V_N = K_S V_S + K_L V_L + K_I V_I \quad (1)$$

where K_L is the partition coefficient of the solute between the gas and liquid phases, V_L is the volume of the liquid phase in the column, and K_S and K_I are respectively the partition coefficients of the solute between the gas phase and the volume, V_S , at the surface of the support surface where the surface forces act, and the volume, V_I , of the zone where the adsorption on the surface of the liquid phase occurs.

From the studies of Martire¹, Waksmundzki *et al.*² and Suprynowicz³, it is known that the adsorption of the solute on the surface of the liquid phase has usually only a small effect on the observed retention volume. Following Musukawa and

Kobayashi⁴, let us define V_s as the volume limited by the geometric surface of the support and by the extent of the adsorption forces, which, according to Harkins and Jura⁵, is no greater than several molecular diameters. It should be noted that this volume is occupied at first by the molecules of the stationary phase. The molecules of the solute enter this region as a result of competitive adsorption, or when the stationary phase is not in close contact with the support and a part of the surface of the support is in contact with the gas phase. It seems that, independent of the extent of contact of the stationary phase with the surface of the support, some of the stationary phase is always within the range of the adsorption forces of the surface of the support and will have different properties to those of the bulk stationary phase. This phenomenon introduces a new element into the problem of the mechanism of adsorption of the solute on the support surface in gas-liquid partition chromatography, for the adsorption can also take place on the surface of the liquid layer whose properties are modified by the adsorption forces of the support. From the investigations of Conder *et al.*⁶ and Giddings⁷, it was shown that such a modified liquid layer is formed when less than 1% of stationary phase is introduced on to a support having a surface area of *ca.* 3 m²/g.

In the present paper, an investigation is reported of the properties of that part of the stationary phase which is situated in the vicinity of the support.

EXPERIMENTAL

Since we did not know a direct method of investigating the properties of the liquid layer situated in the range of the adsorption forces of the support, in the investigations a model system was used with Polsorb C as the solid support. The stationary phases *n*-octadecanol (Koch-Light, Colnbrook, Great Britain) and *n*-octadecane (Fluka, Buchs, Switzerland) were introduced in amounts of 0.2, 0.4, 0.6, 0.8, 1.0, 2.0 and 3.0% (w/w). On the above packings, values of the net retention volume per gram of the column packing, V_{Ng} , were determined for hexane, cyclohexane and carbon tetrachloride at 75.0°. The measurements were made with a Giede GCHF 18.3.6 chromatograph, using a stainless-steel column (2 m × 4 mm I.D.). Hydrogen was used as the carrier gas, and was purified on molecular sieve 5A; the flow-rate of hydrogen was 50 ml/min. Under these conditions, the relations were determined between the V_{Ng} values of the solutes and their partial pressure at the retention maximum. From these relations, the adsorption-energy distribution functions could be obtained for packings containing 0.2% of the stationary phases and for pure Polsorb C.

Since diatomite rock, the raw material from which Polsorb C is produced, occurs as large pieces, slices were made from it and modified in such a way that their surfaces would have analogous properties to those of the surface of Polsorb C. Surface contact angles were then determined for these slices using solutions of the applied stationary phases in chloroform⁸.

RESULTS AND DISCUSSION

In Fig. 1 graphs are presented of the relations between V_{Ng} of hexane, cyclohexane and carbon tetrachloride and the percentage loading of Polsorb C with *n*-

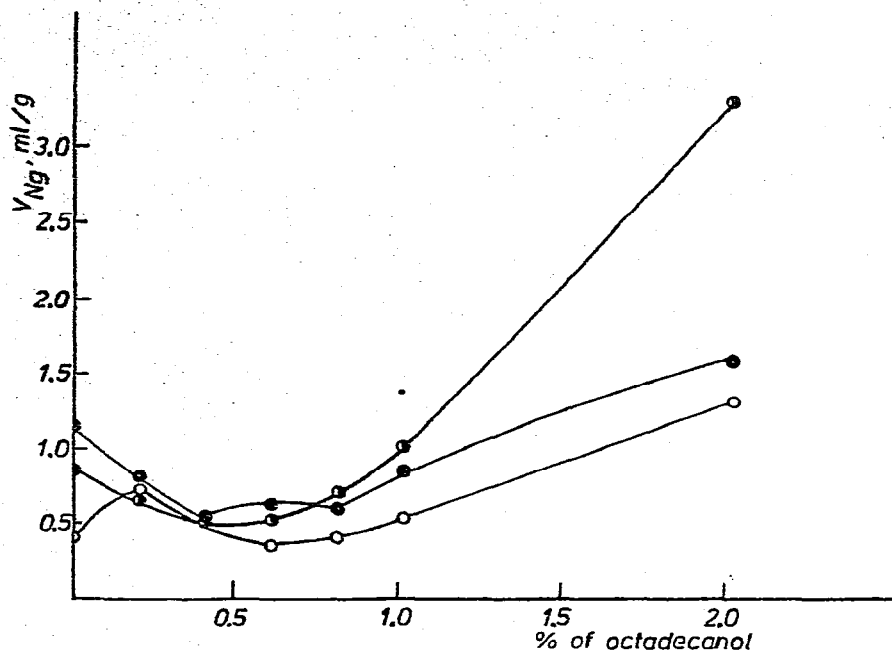


Fig. 1. Graphs of the relation between V_{Ng} and the loading of Porsorb C with *n*-octadecanol for the solutes hexane (O), cyclohexane (●) and carbon tetrachloride (⊙).

octadecanol. It can be seen that for cyclohexane and carbon tetrachloride there is a minimum when the loading is *ca.* 0.5%, while for hexane there is a maximum at 0.2% loading and a minimum at 0.5% loading. These observations can be explained by the formation of a definite structure in the stationary phase on the surface of the support. The properties of the new surface are different from those of pure Porsorb C. It is obvious that the first small quantities of octadecanol orientate their hydroxyl groups toward the surface of the support and that a deactivation and hydrophobization process of adsorption takes place. The retention volumes of the solutes which interact with the surface of Porsorb C in a specific way (carbon tetrachloride and, to a lesser extent, cyclohexane) decrease, for their energy of interaction with the methylated surface is less than that with a surface of pure Porsorb C. Hexane behaves differently. The V_{Ng} value of this compound at 0.2% loading is higher than that with the pure support. This is probably due to an interaction of the hexane molecules with the hydrocarbon chains of octadecanol. The use of a larger amount of octadecanol (*ca.* 0.6%) causes the value of V_{Ng} for hexane to decrease to a value equal to that with the pure support, and the relation between V_{Ng} and the percentage of liquid phase becomes an increasingly monotonic function.

On the basis of the determined relations, we can assume that the molecules of octadecanol are arranged on the surface of the support in a definite order; for small amounts (0.2–0.3%, w/w) of octadecanol there is a layer of molecules in which the hydrocarbon chains are orientated toward the gas phase. The properties of the new surface are similar to those of the polar surface of Porsorb C, which is also occupied with hydroxyl groups. Assuming that one molecule of octadecanol occupies an area

of 22 \AA^2 on the surface of Polsorb C (ref. 9), it can easily be calculated that 0.2% of octadecanol never covers more than *ca.* one third of the surface of Polsorb C ($0.98 \text{ m}^2/\text{g}$). As a result, the layer of alcohol on the support surface cannot be considered as a film which completely covers the surface.

In Fig. 2 the relations are presented between V_{N_2} and the percentage loading of Polsorb C with *n*-octadecane. Minima for cyclohexane and carbon tetrachloride at 0.2% loading show that the non-polar phase also blocks the active centres on the surface of Polsorb C. The newly formed surface is similar to that which originates when Polsorb C is loaded with 0.6% of alcohol, and, in consequence, leads to similar values of retention volume for all solutes chromatographed on the packings containing 0.2% of octadecane and 0.6% of octadecanol. A rapid increase in V_{N_2} on increasing the amount of octadecane in the packing seems to confirm the supposition that the phase does not exist a regular film on the surface of the support but that it is grouped into droplets. Thus the compounds were dissolved in the bulk octadecane phase when the loading was less than 1%.

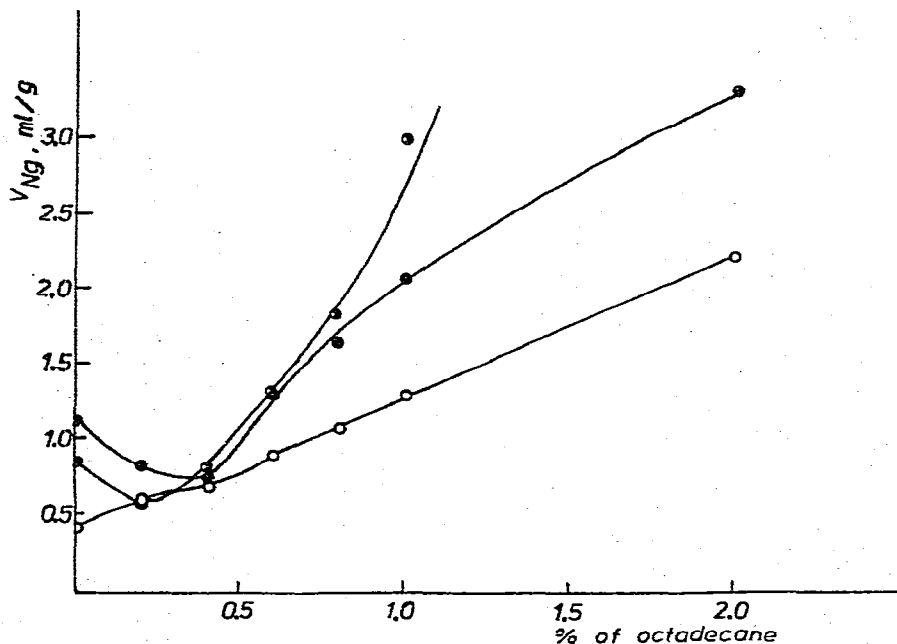


Fig. 2. Graphs of the relation between V_{N_2} and the loading of Polsorb C with *n*-octadecane. Solutes as in Fig. 1.

The suggestion that both the molecules of octadecanol and those of octadecane are orientated on the surface of Polsorb C is confirmed by the results of the measurements of the contact angle for diatomite in solutions of both of the stationary phases. In Fig. 3a the maxima and minima in the graph of the contact angle, θ , against the concentration, c , of *n*-octadecanol can be easily explained by the formation of orientated layers of molecules of octadecanol on the surface of the support. The hydrocarbon chains of the first layer are turned towards the solution, and those of the second layer are directed towards the support. Fig. 3b shows a similar maximum for octadecane at the same concentration at which octadecanol forms a monolayer on

the cut surface. This confirms the previous supposition that octadecane is also orientated on the surface and that its layer has "more hydrophobic" properties than the thicker films obtained at higher concentrations of octadecane. On passing the solutions of stationary phase through the bed of Polsorb C for which the contact angles of the diatomite were measured, it was shown by an extraction method that at the concentrations of the extrema in the graphs in Fig. 3 the support is loaded with 0.2 and 0.6% of the stationary phases, respectively.

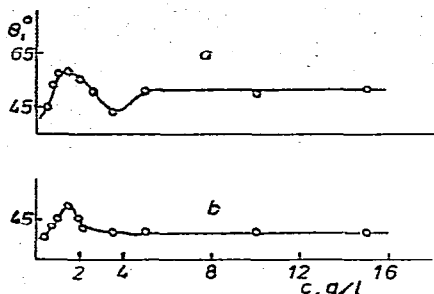


Fig. 3. Graphs of the relation between the contact angle, θ , for the surface of diatomite and the concentration of the stationary phases *n*-octadecanol (a) and *n*-octadecane (b) in chloroform solutions.

The study of the adsorption-energy distribution function for the surface of Polsorb C and the packings containing 0.2% of stationary phase confirms the previous suppositions concerning the distribution of the stationary phase on the support. In Fig. 4a the adsorption-energy distribution function is shown for pure Polsorb C and the solutes cyclohexane and carbon tetrachloride. From this graph, one can distinguish two main regions on the surface which are characterized by peaks at energies of 7.8 and 8.7 kcal/mole. The surface of Polsorb C changes when it is loaded with 0.2% of octadecanol (Fig. 4b). A group of centres is formed having a peak at *ca.* 7.4 kcal/mole and the centres of energy greater than 9 kcal/mole disappear. The value of 7.4 kcal/mole can be ascribed, on the basis of the investigations of Kiselev *et al.*¹⁰, to the interaction of adsorbate molecules with the hydrocarbon chains of octadecanol. The lack of interactions with the strongest centres which are, according to Waks-mundzki *et al.*¹¹, identifiable with the hydroxyl groups of the silica gel situated in the narrowest pores of Polsorb C, shows that these centres are completely blocked by octadecanol. Blocking of the strongest active centres results in a decrease in the average energy of the second group of centres, and in consequence causes the peaks in Fig. 4b to shift toward the lower values of energy (from 8.6 to 8.0 kcal/mole for cyclohexane, and from 8.7 to 8.2 kcal/mole for carbon tetrachloride).

The energetic properties of the surface of Polsorb C change in quite a different way after it is loaded with 0.2% of *n*-octadecane, which, according to the previously described investigations, corresponds to formation of an "orientated" hydrocarbon layer. From Fig. 4c, it can be seen that both carbon tetrachloride and cyclohexane do not interact with methylene groups since there is no peak having energy of *ca.* 7.4 kcal/mole. The strongest centres having energy of greater than 9 kcal/mole are not blocked in this case, while the quantity of active centres within the energy range 7.7–8.6 kcal/mole is considerably decreased. This observation can be explained on the basis of the previous suggestion, that octadecane does not form a film on the surface of Polsorb C but rather that it forms groups of droplets. The surface area of

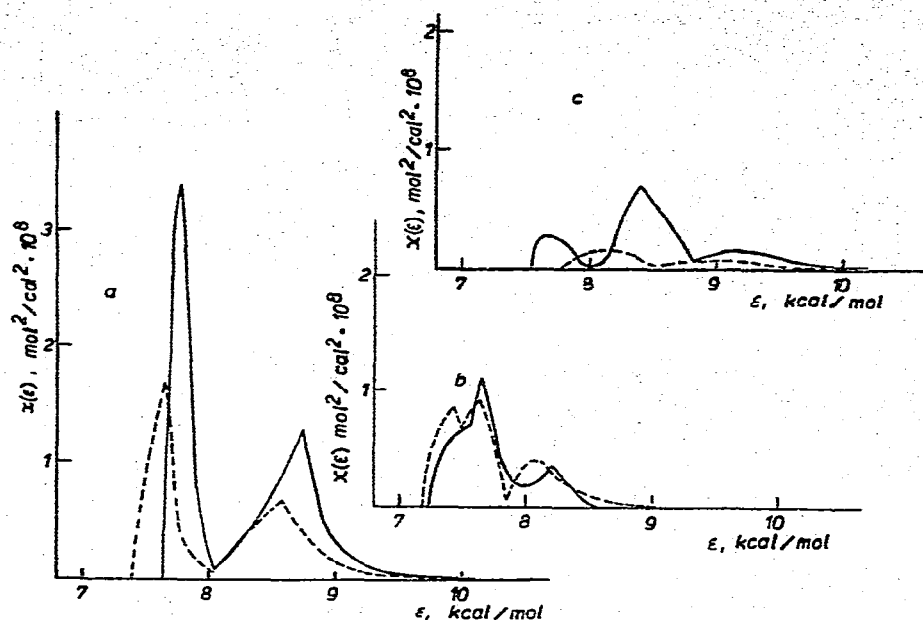


Fig. 4. Adsorption-energy distribution function for (a) the surface of Polsorb C, (b) the surface of Polsorb C loaded with 0.2% of octadecanol and (c) the surface of Polsorb C loaded with 0.2% of octadecane. The solutes were carbon tetrachloride (—) and cyclohexane (---).

such droplets is very small and at the same time both carbon tetrachloride and cyclohexane are very soluble in octadecane; hence the lack of peaks in Fig. 4c corresponding to the adsorption energy of the methylated surface of Polsorb C (ref. 12).

The results of the investigations presented in this paper concerning the properties of packings having small quantities of the stationary phase allow of only a qualitative estimation. Further development of the methods, especially that of determining the adsorption-energy distribution, should allow of a quantitative estimation of the changes in the properties of the solid support under the influence of adsorbed compounds.

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